Introduction

Transition metals have an important place in medicinal biochemistry. Recent advances in medicinal chemistry have made possible the formation of number of transition metal complexes with organic ligands of interest which can be used as therapeutic agents. These complexes offer great diversity of action. They have anti-cancer, anti-inflammatory, anti-infective and anti-diabetic properties. Metal complexes appear to provide a rich platform for the design of novel anticancer drugs. The metal, its oxidation state, the number and types of coordinated ligands and coordination geometry of the complexes can provide a variety of properties. Ligands not only control the reactivity of the metal, but also play critical roles in determining the nature of interactions involved in recognition of biological target sites such as DNA, enzymes and protein receptors.

Schiff bases have a vital position in metal coordination chemistry. The chelating ability of Schiff bases combined with the ease of preparation and flexibility in varying chemical environment about CH=N group makes it an interesting class of ligand in coordination chemistry. Schiff base complexes are very important materials for inorganic biochemists due to their diverse biological [1, 2], pharmacological [3] and antitumor [4-6] activities and their excellent chelating ability. Considerable attention continues to be given to Schiff base ligands and their metal complexes since their properties can be greatly modified through the introduction of different substituents. Design of Schiff base molecules that are capable of binding and cleaving DNA at specific sites has been an area of interest. Schiff base complexes that bind to DNA have been used as diagnostic probes for both structural and functional aspects of nucleic acid in the development of new therapeutic agents [7, 8].

Antipyrine derivatives, being potential oxygen donor ligands, are capable of forming stable complexes with metal ions. Due to easy preparation, rich biological activity and broad spectrum antibacterial [9] and antifungal [10] action, pyrazolone and its complexes received considerable attention in coordination chemistry and medicinal chemistry.

Chromone derivatives have received great attention for their physiological applications. These compounds exhibit wide spectrum of biological properties

including antimicrobial [11], antibacterial, antitumor [12] and antifungal [13, 14] activities.

Scope and objectives of the present study

Extensive studies have been conducted on complexation of Schiff bases with metals due to the attractive physicochemical properties of metal complexes and broad range of utilization in various areas of science. The data available for Schiff bases in literature embrace very wide and diversified subjects comprising vast areas of organo-metallic compounds and multiple aspects of bioinorganic chemistry. Researches based on new Schiff bases and their metal complexes represent one of the most attracting areas of material science, catalysis and chemical research. Although the synthesis and complexation of Schiff bases have been under study for many years, considerable attention continues to be given to these and related metal complexes since their properties can be greatly modified through the introduction of different substituents. Designing of suitable polydentate Schiff base ligands to combine with a metal ion along with a pseudohalide anion has opened a new era of synthesizing metal complexes of particular choice [15]. So with the intention of obtaining information about the coordination chemistry of the metal complexes, it was proposed to study the complexes of Fe(III), Co(II), Ni(II) and Cu(II) ions of two Schiff bases 2,3-dimethyl-4-formyl-[2′-(aminomethyl)pyridine]-1-phenyl-3-pyrazolin-5-one (DFAPP) and ethylenediaminobi (chromone-3-carbaldehyde) (FCED).

The metal salts used are chloride, bromide, iodide, nitrate and perchlorate of Co(II) and Ni(II), chloride, bromide, thiocyanate, nitrate and perchlorate of Fe(III) and chloride, bromide, nitrate and perchlorate of Cu(II).

The complexes were characterized by CHN elemental analysis, spectral techniques like FTIR, UV-visible, EPR, magnetic susceptibility measurements, TG/DTA analysis and single crystal X-ray diffraction technique.

Structure and contents of the thesis

The thesis is presented in five chapters. Chapter I consists an introduction to the work presented in this thesis, scope and objectives of the present work, a discussion of general chemistry, coordination chemistry and electronic and magnetic

properties of Fe(III), Co(II), Ni(II) and Cu(II), applications of Schiff base transition metal complexes and a brief review of literature on studies of Fe(III), Co(II), Ni(II) and Cu(II) complexes derived from pyrazolones and chromones.

Chapter II presents the materials and methods employed for the present study with essential theoretical principles involved in the experimental techniques used. It contains the detailed procedure for the synthesis of Schiff bases.

Chapter III describes the synthesis and characterization of a series of mononuclear complexes of Fe(III), Co(II), Ni(II) and Cu(II) ligated by an antipyrine derived Schiff base 2,3-dimethyl-4-formyl-[2'-(aminomethyl)pyridine]-1-phenyl-3-pyrazolin-5-one (DFAPP). Detailed spectral and structural investigation of the complexes have been carried out. Thermal decomposition stages of the complexes were also studied using TG/DTA**.** In all the complexes DFAPP acts as a neutral bidentate ligand coordinating through pyrazolone carbonyl oxygen and imine nitrogen. The metal to ligand ratio in all the complexes was found to be 1:2. The iron(III) complexes (**1-5**) may be formulated as $[Fe(DFAPP)_2X_2]X$ (where X = Cl^-, Br^- or CNS^-) and $[Fe(DFAPP)_2X]X_2$ (where X = NO_3^- or ClO_4^-). The Fe(III) complexes are found to have a high spin octahedral geometry around central metal ion. TG/DTA analysis shows that all the complexes undergo a two- stage decomposition pattern. The chloride complex is thermally least stable and nitrate complex is most stable among the series. The cobalt(II) complexes (**6-10**) may be formulated as $[Co(DFAPP)_2Cl_2]$ and $[Co(DFAPP)_2]\ X_2$ (where X = Br^-, NO_3^-, ClO_4^-, or I^-). The chloride complex has octahedral geometry while all other complexes have tetrahedral geometry around central metal ion. The thermal decomposition of the complexes exhibit a two-stage decomposition pattern. The iodide complex is thermally least stable and perchlorate complex is most stable among the series. The Ni(II) complexes (**11-15**) may be formulated as $[Ni(DFAPP)_2X_2]$ (where X = Cl^- or Br^-), $[Ni(DFAPP)_2X]X$ (where X = NO_3^- or ClO_4^-)and $[Ni(DFAPP)_2]I_2$. In the series of Ni(II), the chloride, bromide, perchlorate and nitrate complexes have octahedral geometry while iodide complex has tetrahedral geometry around central metal ion. The complexes undergo thermal decomposition in two stages. The perchlorate complex is most stable and chloride complex is least stable among the series. The copper(II) complexes (**16-19**) may be formulated as $[Cu(DFAPP)_2X_2]$ (where X = Br^- or Cl^-)and $[Cu(DFAPP)_2]\ X_2$ (where

X = NO_3^- or ClO_4^-). The geometry around Cu(II) is octahedral in chloride and bromide complexes while it is square planar in nitrate and perchlorate complexes. All the complexes undergo a two stage thermal decomposition pattern. The bromide complex is least stable and perchlorate complex is most stable among the series.

Chapter IV deals with the details regarding the synthesis and characterization of Fe(III), Co(II), Ni(II) and Cu(II) ligated by an chromone derived Schiff base ethylenediaminobi(chromone-3-carbaldehyde) (FCED). Detailed spectral and structural investigation of complexes has been carried out. A few complexes were characterized by single crystal X- ray diffraction technique. Thermal decomposition stages of the complexes were also studied using TG/DTA. Studies shows that FCED acts as a tetradentate ligand chelating through two carbonyl oxygens and two imine nitrogens in all the complexes. The perchlorate complexes undergo explosion when heated to high temperature so it is unable to study their thermal decomposition pattern. The iron(III) complexes (**20**-**24**) may be formulated as $[Fe(FCED)X_2]X$ (where X = Cl^-, Br^- or CNS^-) and $[Fe(FCED)X]X_2$ (where X = NO_3^- or ClO_4^-). All the complexes have an octahedral geometry around central metal ion and complexes undergo a two stage thermal decomposition pattern. The cobalt(II) complexes (**25**-**29**) may be formulated $[Co(FCED)]X_2$ (where X = Cl^-, Br^- or I^-) and [Co(FCED)X]X (where X = NO_3^- or ClO_4^-). Among the complexes chloride, bromide and iodide complexes have tetrahedral geometry while nitrate and perchlorate complexes have octahedral geometry around central metal ion**.** All the complexes undergo a two stage thermal decomposition pattern. The nickel(II) complexes (**30**-**34**) may be formulated as [Ni(FCED)X]X (where X = Cl^-, I^- or ClO_4^-) and $[Ni(FCED)(H_2O)_2]X_2.H_2O$ (where X = NO_3^- or Br^-). The chloride, perchlorate and iodide complexes have a square pyramidal geometry around central metal ion while bromide and nitrate complexes have an octahedral geometry around central metal ion. The chloride, iodide and perchlorate complexes undergo a two stage thermal decomposition pattern while bromide and nitrate complexes undergo a three stage thermal decomposition pattern.

The bromide (**31**) and (**32**) nitrate complexes were characterized by single crystal XRD. The complexes **31** and **32** were crystallized in the monoclinic system with space group P21/1. The crystal structure of **31** and **32** reveals that both the complexes are isostructural. The nickel(II) ion in both the complexes is coordinated by neutral

tetradentate ligand FCED and two water molecules. The equatorial positions of Ni(II) metal center are occupied by two carbonyl oxygen atoms and two imine nitrogen atoms of tetradentate chelating ligand while trans axial positions are occupied by oxygen atoms from two water molecules. Thus FCED forms a six membered chelate ring around Ni(II) metal center. In complexes **31** and **32** both the anions (bromide and nitrate respectively) remain as counter ion. In both the complexes Ni(II) centre exhibits slightly distorted octahedral geometry. Each fragment of the complex contains one molecule of hydrated water. A hydrogen bond scheme is present in both complexes interlinking hydrogen atoms of coordinated water molecules with counter ions and crystal bound water. These hydrogen bonds are mainly responsible for supramolecular network. Intermolecular hydrogen bonds present in crystal of complexes form one dimensional chain structure and adjacent chains are connected by intermolecular hydrogen bonds to form an infinite double chain structure.

The copper(II) complexes (**35-38**) may be formulated as [Cu(FCED)X]X (where X = Cl^-, Br^- or NO_3^-) and [Cu(FCED)]X_2 (where X = ClO_4^-). All the Cu(II) complexes except perchlorate complex have a square pyramidal geometry while perchlorate complex has a square planar geometry around central metal ion. The bromide and nitrate complexes undergo thermal decomposition in two stages while chloride complex decomposes in three stages.

The nitrate complex has been characterized by single crystal XRD. The complex was crystallized in the monoclinic system with space group P21/n. Each copper atom is penta-coordinated with square pyramidal geometry around copper centre. The copper(II) centre is coordinated by two carbonyl oxygen atoms (O1,O2) and two imine nitrogen atoms (N1,N2) of tetradentate chelating ligand FCED while the fifth position is occupied by monodentately coordinated nitrate ion. The value of trigonal index indicates the existence of a distorted square pyramidal metal coordination sphere. The complex is involved in weak π-π interactions with the carbon atoms present in the adjacent chromone ring via C(7)---C(17) interaction resulting in the formation of a dimer. Each dimer extent to form 3D stacks through weak hydrogen bond interactions *via.* ionic as well as coordinated nitrates which results in herringbone picking network.

Summary and Conclusion

Two Schiff base ligands and thirty eight metal complexes with Fe(III), Co(II), Ni(II) and Cu(II) have been successfully synthesized and characterized. The results revealed that the nature of ligand, metal ion and counter ion play important roles in determining the structure and topology of complexes. The thermal decomposition pattern of all the complexes was studied. The X-ray crystal analysis of **31** and **32** shows that the nickel(II) ion is in a distorted octahedral environment with the metal atom ligated by N_2O_2 from the ligand at the equatorial positions and two aqua ligands in axial positions. Intermolecular hydrogen bonds are present in crystal of complexes **31** and **32** to form one dimensional chain structure and adjacent chains are connected by intermolecular hydrogen bonds to form an infinite double chain structure. The X-ray crystal analysis of **37** shows that the copper(II) ion is in a distorted square pyramidal environment with the metal atom ligated by N_2O_2 from the ligand at the equatorial positions and the fifth, apical donor is one oxygen atom from nitrate ion. The individual complex molecules are stacked together to form one dimensional infinite zig-zag molecular chains by intermolecular π-π stacking interactions between pairs of chromone rings. The findings of structural studies are interesting in that the Schiff base ligands can control the stereochemistry of complexes and provide us numerous examples of different geometries around central metal ion.

References

[1] Q.B. Li, L.W. Xue, W.C. Yang, G.Q. Zhao, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, 43 (**2013**) 1471.

[2] G.B. Bagihalli, P.G. Avaji, S.A.Patil, P.S. Badami. *Eur. J. Med. Chem.*, 43 (**2008**) 2639.

[3] K. Singh, M.S. Barwa, P. Tyagi, *Eur. J. Med. Chem.*, **41**, (**2006**) 147.

[4] X. Zhong, H.L. Wei, W.S. Liu, D.Q. Wang, *Bioorg. Med. Chem. Lett*., 17, (**2007**) 3774.

[5] N. Shahabadi, S. Kashanian, F, Darabi. *Eur. J. Med. Chem.*, 45, (**2010**) 4239.

[6] X. Qiao, Z.Y. Ma, C.Z. Xie, F. Xue, Y.W. Zhang, J.Y. Xu, Z.Y. Qiang, J.S. Lou, G.J. Chen, S.P. Yan, *J. Inorg. Biochem*., 105, (**2011**) 728.

[7] J. Tan, B. Wang, L. Zhu, *Bioorg. Med. Chem*., 17 (**2009**) 614.

[8] V.P. Sondhiya, R.N. Patel, D.K. Patel, K.K. Shukla, Y. Singh, *Int. J. Med. Pharm. Sci.*, 2(2) (**2012**) 10.

[9] B. Anupama, C. Gyanakumari, *Res. J. Pharma. Bio. Chem. Sci*., 2, (**2011**) 140.

[10] S. Sobha, N. Raman, *Int. J. Pharma. Bio. Sci*., 3, (**2012**) 2.

[11] F. Arjamand, F. Sayeed, M. Muddassir. *J. Photoch. Photobio.* ***B,*** 45 (**2011**) 166.

[12] F.A. Yakout, *Egypt. J. Chem*., 45(**2004**)1029.

[13] K.M. Khan, N. Ambreen, U.R. Mughal, S. Jalil, S. Perveen, M.I. Choudary, *Eur. J. Med. Chem*., **45** (**2010**) 4058.

[14] T. E. Ali, S.A. Aziz, H.M.E. Shaaer, F. I. Hanafy, A. Z. Fauomy. *Turk. J. Chem*., 32 (2008) 365.

[15] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bocchman, *Advanced Inorganic Chemistry*, Sixth edn., Wiley, Newyork. (**1999**)